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PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
(SECTION A)

Part 4]

1946

[Volume 15

A STUDY OF THE NOCTURNAL VARIATION IN THE
INTENSITY OF THE ZODIACAL LIGHT AT AGRA

BY JAGDEO SINGH

BALWANT RAJPUT COLLEGE, AGRA †

Communicated by Prof. R. K. Asundi. Received on April 15, 1946

INTRODUCTION

The Zodiacal light is a tongue of light observed after sun-set in the west, or before the dawn in the east, in different seasons of the year. Sometimes it is seen inclined to the horizon and, in some of the seasons, it is found to be vertical, fading in intensity from the base upwards extending upto 50 or 60 degrees above the base. Fath's¹ spectroscopic studies show the presence in it of sunlight with the characteristic Fraunhofer's lines. Later studies by various investigators² show also the presence of the auroral green line of oxygen at $\lambda 5577$ and the first positive bands of nitrogen. These observations are taken as evidence for the conclusion that the Zodiacal light is sun-light scattered by some types of particles, superimposed by the light from the night-sky. A study by Dufay of the state of polarization of the zodiacal light, shows that it is plane polarized to the extent of 15 per cent, whereas the light of the night-sky indicates only a 2 to 4 per cent polarisation. This shows that the slight polarisation of the night-sky is due to the super position to some extent of the zodiacal light on it.

† At present in Benares Hindu University.

A study of the intensity variation of zodiacal light has been made by Elvey and Roach³ in France, using a photoelectric recording photometer, and its variation studied from season to season and from latitude to latitude. Nocturnal variation of the light intensity has also been observed. It is also reported by many observers that some times a sudden change of intensity is observed; and its source is traced to either the presence of magnetic storms or solar outbursts or to presence of water vapour in the upper atmosphere or to meteoric activities⁴ near about the Sun. The present author⁵ made some visual observations on the nocturnal variation of the intensity of zodiacal light at Poona during March and April 1943. This year, he has made a similar study of the West Zodiacal light in the months of March and April, 1947, from the top of a house (Mehtab Bhawan), some 30 feet high, at Wazir Pura, Agra. The intensity variations are now observed by means of a modified photometer of the type employed by Chipлонkar⁶ for measuring the intensity of the Zenith sky.

EXPERIMENTAL

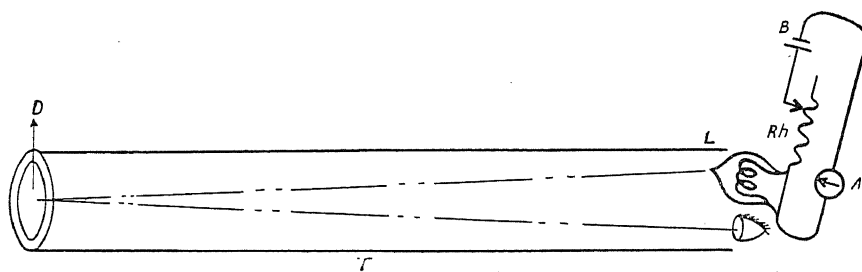


Fig. 1

The photometer consists of a cylindrical tube T (Fig. 1), made of black unglazed paper, 2.7 cms. in internal diameter and 19.5 cms. in length. In the centre of one end of the tube is fixed, by means of a fine wire, a brass disc D 1.7 cms. in diameter. This is coated with magnesium oxide on the surface inside the tube, leaving an uncovered annular space around it. It is illuminated by a motor car bulb L, in which a variable current can be passed from a battery 'B,' in series with an adjustable Rheostat 'Rh' and with a suitable ammeter 'A.' The bulb is

calibrated first against a source of one candle power for different currents by the help of a grease spot photometer, and the corresponding value of 'r' is found. The albedo of the magnesium oxide is taken to be 0.97. The tube is directed towards the centre of the base of the zodiacal light cone which illuminated the annular space in the farther end of the tube. The disc is now illuminated by the bulb, and its illumination adjusted by varying the current in the bulb until the two match, when the current is noted down. The current is converted into the intensity in candle-2 cms, and the time of observation is converted into the depression of the sun below the horizon. The Zodiacal light stands out quite distinctly from the rest of the sky light, when the depression is near about 14° . The intensity is, therefore, measured from the time when the depression is 10° , and continued till it is 24° . After this, the light became very faint.

RESULTS AND DISCUSSIONS

TABLE I

N. B. Dots on integers represent the negative sign.

Log₁₀ of Intensity for the month of March.

S. No.	Depres- sion.	days	14-3-47	15-3-47	16-3-47	17-3-47	18-3-47	19-3-47	21-3-47	22-3-47	Mean.
1	11° 15'	...	5.4065	6.7218	6.4518	6.2455	6.4518	5.1038	6.4518	6.6904	
2	12° 30'	6.4518	6.0899	6.0899	6.4518	6.0899	7.9480	6.7218	6.2455	6.2611	
3	13° 45'	6.2455	7.9880	6.0899	6.0899	6.0899	7.9480	6.2455	6.0899	6.0983	
4	15°	7.9480	7.8267	7.9480	7.9480	7.9480	7.8882	6.0899	7.9480	7.9431	
5	16° 15'	7.9480	7.7235	7.8267	7.8882	7.9480	7.7235	7.9480	7.8882	7.8617	
6	17° 30'	7.8267	7.7235	7.8267	7.8267	7.8267	7.7235	7.8267	7.8267	7.8009	
7	18° 45'	7.7716	7.7235	7.7235	7.7716	7.7716	7.7235	7.8267	7.7716	7.7604	
8	20°	7.7716	7.6345	7.6762	7.7235	7.7235	7.7235	7.7235	7.7716	7.7185	
9	21° 15'	7.7716	...	7.6762	7.6762	7.7235	7.7716	7.7716	7.7716	7.7374	
10	22° 30'	7.7235	...	7.6345	7.6762	7.7235	7.6345	7.7235	7.7235	7.6913	
11	23° 45'	7.7235	...	7.7235	7.7235	7.7235	

TABLE 2

log₁₀ of the Intensity of the Zodiacal light for April.

S. No.	depression	8-4-47	9-4-47	10-4-47	11-4-47	12-4-47	13-4-47	14-4-47	15-4-47	Mean.
1	11°	...	6.4518	6.7218	5.1038	6.0899	6.1614	6.2455	5.1038	6.5540
2	12°	6.4518	6.2455	6.2455	6.2455	6.0899	...	6.0152	6.4518	6.2492
3	13°	6.0899	6.1618	6.0899	6.0899	7.9480	...	7.9480	6.0899	6.0596
4	14°	6.0152	7.9480	6.0152	6.0899	7.8882	7.8882	7.8267	7.9480	7.9524
5	15°	7.8882	7.8882	7.9480	7.9480	7.8267	7.8267	7.8267	7.9480	7.8876
6	16°	7.8267	7.8882	7.8267	7.8267	7.7716	7.7716	7.7716	7.8267	7.8137
7	17°	7.7716	7.8267	7.8267	7.8267	7.7235	7.7716	7.7235	7.8267	7.7871
8	18°	7.7235	7.7716	7.7235	7.7716	7.7235	7.7716	7.7235	7.8267	7.7544
9	19°	7.7235	7.7235	7.7235	7.7235	7.7235	7.6762	7.7235	7.7716	7.7236
10	20°	7.7235	7.7235	7.7235	7.7235	7.7235	...	7.6762	7.7716	7.7236
11	21°	7.6762	7.7235	7.7235	...	7.7235	7.7716	7.7236
12	22°	7.6762	7.6345	7.7235	7.6781

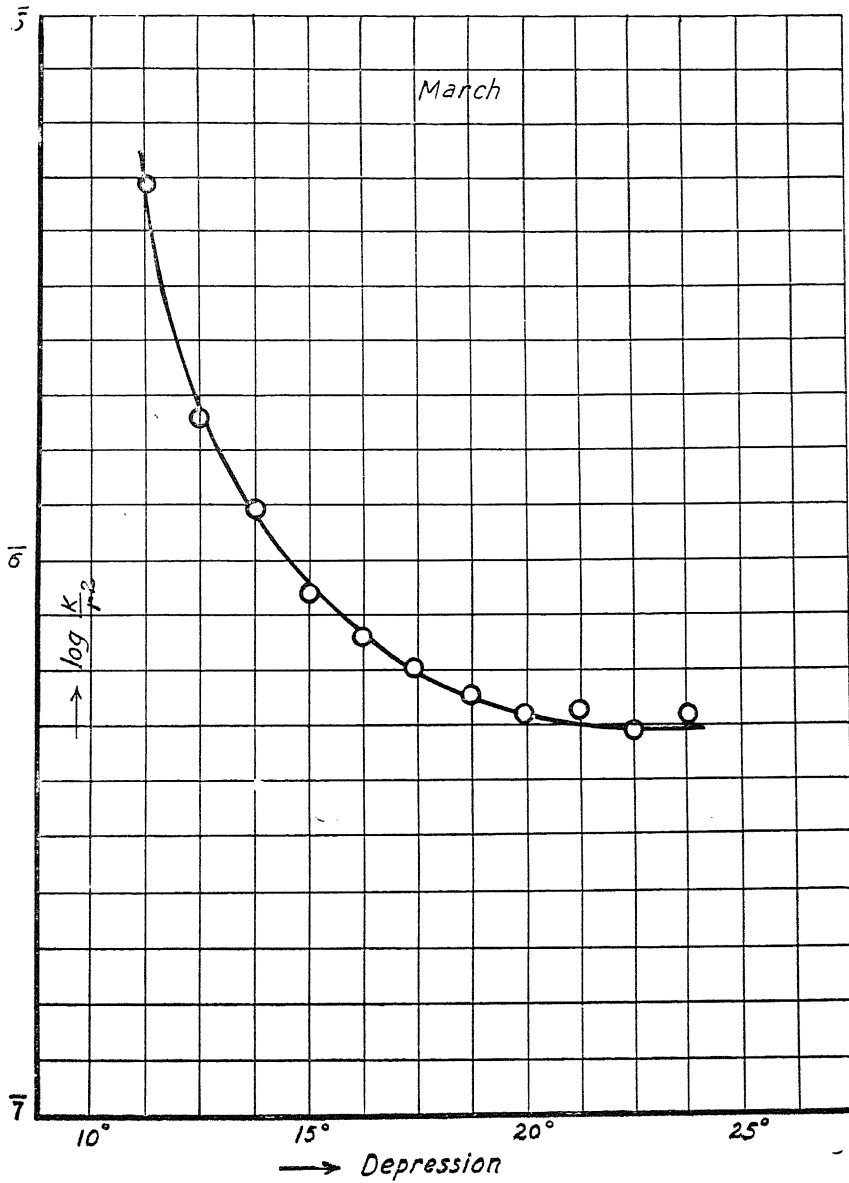
TABLE 3

log₁₀ of the Intensity of the Nightsky near about the North Pole.

S. No.	depression.	8-4-47	9-4-47	10-4-47	11-7-47	12-4-47	13-4-47	14-4-47	15-4-47	Mean
1	11°15'	...	6.2455	6.2455	6.4518	6.0152	...	7.9480	6.2455	6.1919
2	12°15'	6.2455	6.0899	6.0152	6.0899	7.9880	...	7.9480	6.0899	6.0666
3	13°15'	7.9480	6.0152	7.9480	7.9480	7.8267	...	7.8267	7.9480	7.9229
4	14°15'	7.8882	7.8882	7.8882	7.8267	7.7716	7.8267	7.7716	7.8882	7.8437
5	15°15'	7.8267	7.8267	7.8267	7.8267	7.7235	7.7716	7.7716	7.8267	7.8000
6	16°15'	7.7716	7.7716	7.7716	7.7716	7.7235	7.7235	7.7235	7.7716	7.7536
7	17°15'	7.7235	7.7235	7.7235	7.7716	7.6762	7.7235	7.6762	7.7716	7.7112
8	18°15'	7.7235	7.7235	7.6762	7.7235	7.6345	7.6762	7.6345	7.7235	7.6894
9	19°15'	7.7235	7.6762	7.6345	7.6762	7.6762	7.6762	7.6345	7.7235	7.6776
10	20°15'	7.7235	7.6762	7.6345	7.6762	7.6345	7.6762	7.6701
11	21°15'	7.6762	7.6762	7.6345	...	7.6345	7.6762	7.6595

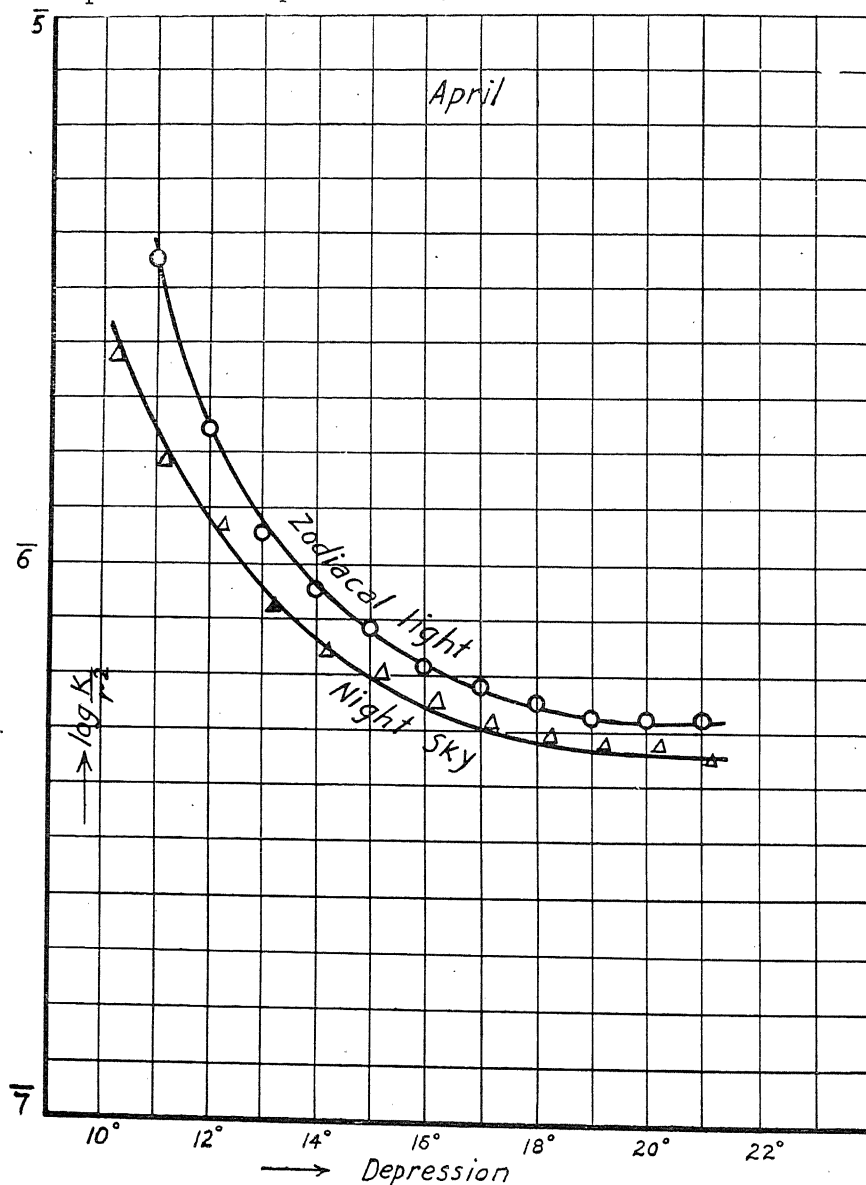
Table 1 gives the log₁₀ of the intensity of the Zodiacal light on different days for the month of March, 1947, on moonless nights for

different angles of depression of the sun. Table 2 gives the same for the month of April, and Table 3 gives the \log_{10} of the intensity of the night-sky round the polestar. This was also measured in a similar way.



Graph 1 shows relation between the \log_{10} of the mean value of the intensity and the angle of depression for the month of March, 1947. The

ordinate represents the \log_{10} of the mean intensity, and the abscissae the angle of depression. Graph 2 similarly shows the same relation for the



month of April. On this is also shown the \log_{10} of the intensity of the night-sky near about the polestar.

From this study of the intensity of the Zodiacal light, the following facts are brought about :

1. The nature of the variation of the intensity with the angle of depression on every night remains practically the same.
2. There is some slight variation from night to night for the same angle of depression.
3. The variation in intensity of the Zodiacal light is of the same nature as that of the night sky at the same time and on the same days near about the region of the polestar.
4. The mean intensity of the Zodiacal light for the month of March is greater than that for the month of April for the same angles of depression.
5. The intensity of the night sky near the polestar is systematically less than that of the Zodiacal light for the same angles of depression.

There are two theories to explain the observations of the phenomenon of the Zodiacal light, namely the Planetary theory, as put forward by Nolke, James Jeans, Moulton etc., and the Atmospheric theory, as put forward by Schmid^{7, 8}, Hulburt, Vegard etc. In the planetary theory, it is assumed that the particles, from which the light is scattered, are a part of the solar system. These particles are assumed to be fairly big in size as compared to air, and they are held near about the sun due to its gravitational pull. In the atmospheric theory, it is assumed that the light is scattered from the earth's atmosphere; it exists in the form of a lens round the earth, extending hundreds of miles above the earth's surface. The time variation of the intensity of Zodiacal light and its similarity with that of the night sky near about the pole-star, probably support the atmospheric theory.

My thanks are due to Dr. R. K. Asundi, Benares Hindu University, for his interest in the work.

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MEASUREMENT OF ACOUSTIC IMPEDANCE

BY SHYAM BEHARI LAL SRIVASTAVA

(Communicated by Dr. R. N. Ghosh, D. Sc., University of Allahabad

Received on September 14, 1946.)

The present paper is intended to give a short account of the method of quick determination of Acoustic Impedance of 'felt' and 'celotex', and its variation with frequency.

INTRODUCTION

On account of growing interest in the measurement of Acoustic Impedance for commercial purposes, we need an apparatus which may readily determine the absorption coefficient, phase change etc. with a fair degree of accuracy.

In this laboratory, various experiments have been performed by Mohammed, Verma and Chandra Kanta, for the determination of these quantities; but the one, described in the sequel, gives fairly accurate values and allows their quick determination.

The principle, underlying this method, is to produce standing waves inside a sound-tube and to locate nodes and antinodes by means of telephone receiver. The maxima and minima of sound are located, after amplification, by a voltmeter which is connected to the output terminals of the amplifier through a copper-oxide-rectifier.

II. EXPERIMENTAL

The entire assembly of the apparatus consists of

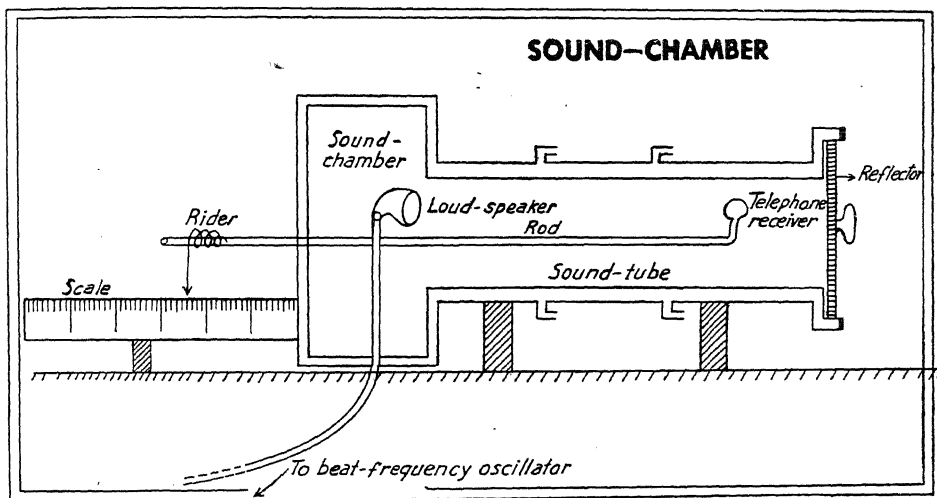
- (i) Sound-chamber.
- (ii) Source of sound (Beat frequency oscillator).
- (iii) Telephone receiver.

In order to present a vivid picture of the experimental technique, a short description of each of the above three equipments will be given.

A Sound-tight chamber is carefully fitted to one end of a long clay-pipe having grooves at the other end. The perfect reflector or any

piece of acoustic material, cut to the size of the groove closes this end.

A loudspeaker, kept inside the sound-tight chamber and fed by a beat frequency oscillator, acts as a source of sound.

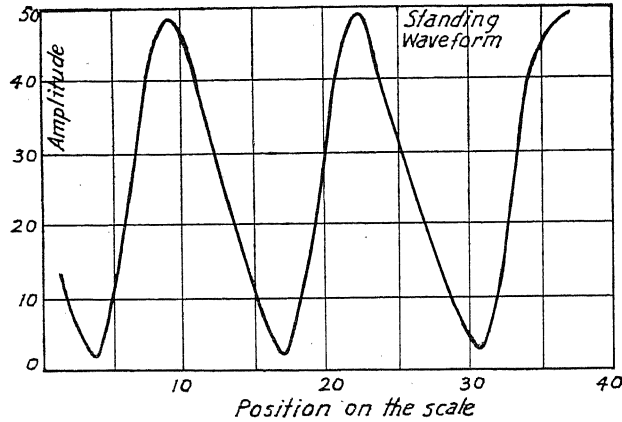


The telephone receiver is connected to the input terminals of a Phillip amplifier. The detector consists of a 10 volt-range voltmeter, connected to the out put terminals of the amplifier through a copper-oxide rectifier.

A well defined standing-wave pattern leads to the accuracy of the result. To accomplish this, the perfect reflector (brass disc $\frac{1}{4}$ " thick) is put at the grooved end of the sound-tube. The position of the telephone receiver is altered in regular steps along the radius of the tube, and the corresponding deflections in the voltmeter are noted. A graph, plotted between the scale readings and the voltmeter readings, is the required standing waveform.

Now coming to the main part of the experiment, *i.e.*, the determination of acoustic impedance, only a quick and simple procedure is left. The perfect reflector at the groove is replaced by the specimen. Knowing the positions and the amplitudes of the first maxima nearest the reflector end, for the two cases, an application of the simple formulae, quoted below, gives the required values. The shift of maximum, (*i.e.*, the difference of scale readings between the first maximum for the specimen and that

for the perfect reflector), enables one to calculate phase change after reflection.



III. THEORY

Let ξ_1 and ξ_r be the incident and the reflected particle velocities, then

$$\xi_1 = e^{jk(ct-x)}$$

$$\xi_r = -\beta e^{-2jkl_0} e^{jk(ct+x-2l)}$$

where ' β ' is the reflection coefficient and $2jkl_0$ is the phase change after reflection.

' l_0 ' is the shift of maximum.

' l ' is the length of the sound-tube.

The resulting pressure and velocity are given by

$$p = Z_0 \left\{ e^{jk(ct-x)} + \beta e^{-2jkl_0} e^{jk(ct+x-2l)} \right\}$$

$$u = e^{jk(ct-x)} - \beta e^{-2jkl_0} e^{jk(ct+x-2l)}$$

The resultant amplitude of pressure is

$$P_x^2 = 1 + \beta^2 + 2\beta \cos 2k(l^1 - x)$$

$$\text{where } l^1 = l + l_0.$$

$$\text{Thus, } P_{\max} = 1 + \beta$$

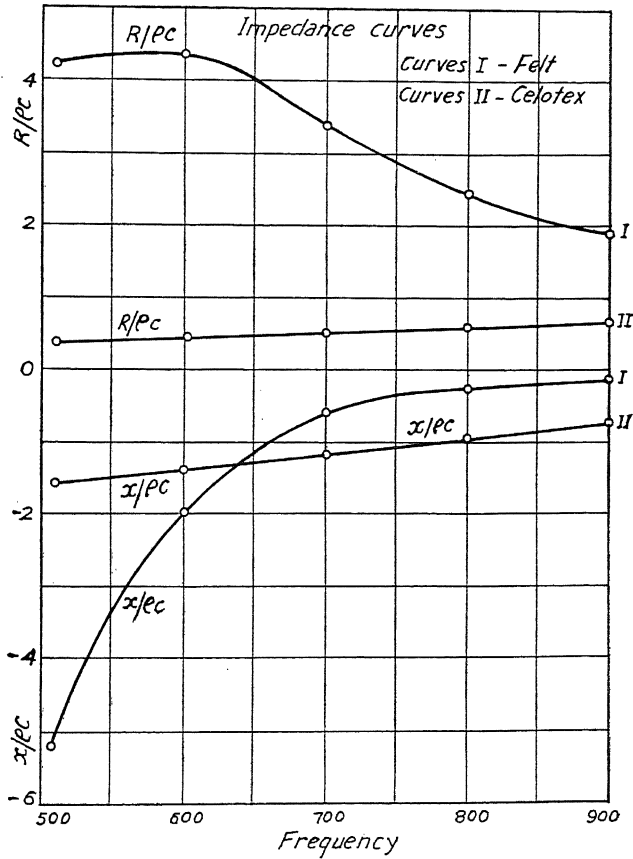
$$P_{\min} = 1 - \beta.$$

and

$$\frac{P_{\max}}{P_{\min}} = \frac{1+\beta}{1-\beta} = \frac{i_1}{i_2}$$

where i_1 and i_2 are voltmeter deflections at maxima and minima respectively.

The resistance and the reactance terms of the Acoustic Impedance are given by



$$\frac{R}{\rho c} = \frac{1 - \beta^2}{1 + \beta^2 - 2\beta \cos 2kl_0}$$

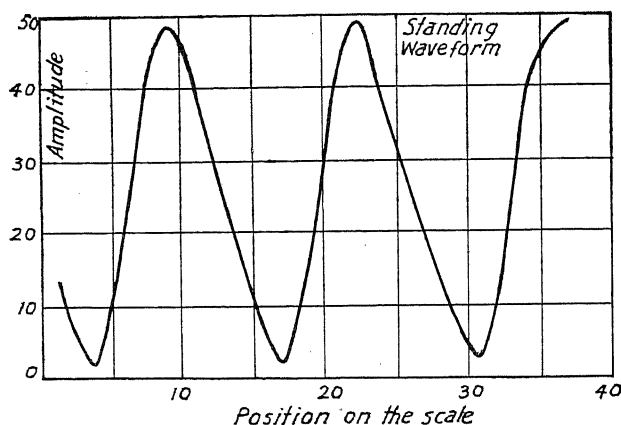
$$\frac{X}{\rho c} = \frac{-2\beta \sin 2kl_0}{1 + \beta^2 - 2\beta \cos 2kl_0}$$

IV. RESULT

The variation in the reactive and the resistive terms of Impedance of 'Felt' and 'Celotex', with frequency are shown in the above graph.

The following tables (I to IV) give the experimental observations, while tables V and VI give the calculated values of Impedance of 'Felt' and 'Celotex.'

for the perfect reflector), enables one to calculate phase change after reflection.



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Let ξ_1 and ξ_r be the incident and the reflected particle velocities, then

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$$\xi_r = -\beta e^{-2jkl_0} e^{jk(ct+x-2l)}$$

where ' β ' is the reflection coefficient and $2jkl_0$ is the phase change after reflection.

' l_0 ' is the shift of maximum.

' l ' is the length of the sound-tube.

The resulting pressure and velocity are given by

$$p = Z_0 \left\{ e^{jk(ct-x)} + \beta e^{-2jkl_0} e^{jk(ct+x-2l)} \right\}$$

$$u = e^{jk(ct-x)} - \beta e^{-2jkl_0} e^{jk(ct+x-2l)}$$

The resultant amplitude of pressure is

$$P_x^2 = 1 + \beta^2 + 2\beta \cos 2k(l^1 - x)$$

$$\text{where } l^1 = l + l_0.$$

$$\text{Thus, } P_{\max} = 1 + \beta$$

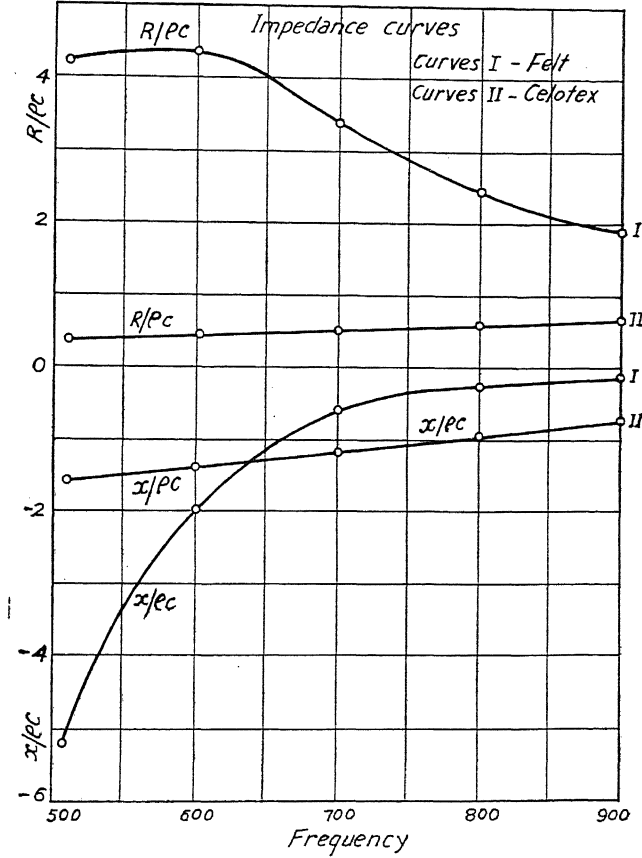
$$P_{\min} = 1 - \beta.$$

and

$$\frac{P_{\max}}{P_{\min}} = \frac{1+\beta}{1-\beta} = \frac{i_1}{i_2}$$

where i_1 and i_2 are voltmeter deflections at maxima and minima respectively.

The resistance and the reactance terms of the Acoustic Impedance are given by



$$\frac{R}{\rho c} = \frac{1 - \beta^2}{1 + \beta^2 - 2\beta \cos 2kl_0}$$

$$\frac{X}{\rho c} = \frac{-2\beta \sin 2kl_0}{1 + \beta^2 - 2\beta \cos 2kl_0}$$

IV. RESULT

The variation in the reactive and the resistive terms of Impedance of 'Felt' and 'Celotex', with frequency are shown in the above graph.

The following tables (I to IV) give the experimental observations, while tables V and VI give the calculated values of Impedance of 'Felt' and 'Celotex.'

TABLE I

Positions and Amplitudes of Maxima and Minima—Perfect Reflector.

Position on the scale (inches)	Amplitude	Position	Amplitude	Position	Amplitude
1	14	13	23	25	32
3	3	15	12	27	19
3.4	2	17	2	29	8
5	13	19	19	30.5	3
7	39	21	43	31.0	5
9	49	22.2	49	33	26
11	39	23.0	46	35	44
				37	49

TABLE II

Amplitude of the 1st Maximum and Position and Amplitude of the 1st Minimum—Imperfect reflectors.

Amplitude of the 1st Minimum

Material	Amplitude of 1st Maximum	With source of sound	Without source of sound	Amplitude (Minimum)	Position of the 1st Minimum
Felt	62	6.0	2.0	4.0	2.85"
Celotex	98	8.0	2.0	6.0	3.75"

TABLE III

Position of 1st Maximum and 1st Minimum at various frequencies—Perfect Reflector.

Frequency cycles/sec.	Position of 1st Maximum	Position of 1st Minimum
512	13.2"	9.3"
600	10.7"	7.9"
700	9.5"	6.8"
800	7.7"	5.5"
900	7.5"	5.2"

TABLE IV

Positions and Amplitudes of 1st Maximum and 1st Minimum at various frequencies—for Felt and Celotex.

Material	Frequency cycles/sec.	Amplitude of First Maximum	Position of First Maximum	First Minimum			
				Ampli- tude with source of sound	Ampli- tude with- out sound	Ampli- tude at Mini- mum	Position on the scale
Felt	512	46	12.7	5	1	4	8.8"
	600	25	10.3	4	1	3	7.5"
	700	19	9.1	6	1	5	6.4"
	800	10	7.3	4.5	1	3.5	5.1"
	900	7	7.1	4.0	1	3.0	4.8"
Celotex	512	76	12.0	7.0	3	4	8.1"
	600	48	9.7	5	2	3	6.9"
	700	31	8.5	5	3	2	5.8"
	800	26	7.0	5	3	2	4.8"
	900	21	6.7	5	3	2	4.4"

TABLE V

Absorption coefficient, Reflection coefficient, Shift of Maximum, Reactance and Resistance terms of Impedance at various frequencies—Felt.

Frequency cycles/sec.	Absorption coefficient ($1 - \beta^2$)	β^2	Reflection coefficient ' β '	Shift of Maximum ' l_0 '	Resistance $\frac{R}{\rho c}$	Reactance $\frac{X}{\rho c}$
512	.294	.706	.84	0.5"	4.2	-5.2
600	.395	.605	.77	0.4"	4.3	-2.0
700	.678	.322	.57	0.4"	3.4	-0.56
800	.816	.184	.43	0.4"	2.4	-0.24
900	.888	.112	.33	0.4"	1.9	-0.13

TABLE VI

Absorption coefficient, Reflection coefficient, Shift of Maximum, Reactance and Resistance terms of Impedance at various frequencies—Celotex.

Frequency cycles/sec.	Absorption coefficient ($1 - \beta^2$)	β^2	Reflection coefficient ' β '	Shift of Maximum ' l_0 '	Resistance $\frac{R}{\rho c}$	Reactance $\frac{X}{\rho c}$
512	.199	.801	.895	1.2"	0.36	-1.6
600	.231	.769	.876	1.0"	0.46	-1.4
700	.250	.750	.866	1.0"	0.48	-1.2
800	.296	.704	.836	0.7"	0.58	-0.9
900	.364	.636	.797	0.8"	0.64	-0.73

I take this opportunity to offer my sincere thanks to Dr. R. N. Ghosh, D. Sc, F. N. I., for his helpful suggestion of the problem and for the active interest he has taken in the work. My thanks are also due to Dr. R. N. Rai of Delhi University and Dr. D. Sharma of Allahabad University for their favours of having gone through the manuscripts.

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STUDIES IN THE AMPHOTERIC NATURE OF HYDRATED STANNIC OXIDE AND THE DETERMINATION OF ITS ISOELECTRIC POINT

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Two forms of stannic oxide, α and β , are recognised for a long time. The former variety is obtained by precipitation from a solution of stannic salt by alkali lye or ammonia solution. The precipitated oxide is soluble both in acids and alkalis, which suggest its amphoteric nature. The adsorptive capacity of hydrated stannic oxide as a mordanting agent is too well known. The adsorption of ferro-cyanide radical by stannic hydroxide obtained as a result of hydrolysis by ageing of a solution of stannic chloride was noted by Lowenthal¹, as early as in 1852, and Mecklenburg² and Lorenz³ studied this quantitatively. The removal of phosphate by the β -form of the oxide, was ascribed by Mecklenburg to be due to the adsorption of phosphate by the oxide, which depends greatly on the mode of the formation of stannic oxide precipitate.

In the course of the study⁴ of the complex formations between a freshly prepared stannic oxide with soluble oxalates and oxalic acid, it was interesting to observe, that whilst the former formed complexes very easily, the adsorption of oxalate from its dilute solutions, where no precipitate dissolved due to complex formation, by the hydrated oxide, was negligible. On the other hand, the formation of complex was not so remarkable with oxalic acid, though sufficient amounts of oxalate ions were adsorbed with the precipitate. In view of these observations, it is clear that the adsorption of the anion or the cation by hydrated stannic oxide, is related to the hydrogen ion concentration of the medium. It is well recognised in the cases of such amphoteric bodies like proteins, that the adsorption of a cation or an anion depends on the hydrogen ion concentration of the medium in which the protein is suspended. Thus Loeb⁵

has shown that a protein like gelatin takes up silver ions from silver nitrate solution, when the pH value of the solution is greater than 4.7, and it takes up ferrocyanide ions, when the pH is less than this value, which is that for the isoelectric point of gelatin.

In this paper stannic oxide was precipitated by the addition of ammonia to a solution of stannic chloride at a room temperature of 25°C. The hydrated oxide, thus obtained, was voluminous in character and it was washed with distilled water, till it was free from ammonia and a large majority of the chloride. As on further washing, the hydroxide had a tendency to pass in a colloidal state, complete removal of chloride was thus not possible. The object of this investigation was to study the amphoteric nature of the hydrated oxide, as related to the adsorption of a cation or of an anion from an added electrolyte. It is well known, that substances of basic character adsorb hydrogen ions and anions, while those of acid character have a remarkable preferential adsorption for hydroxyl ions and cations.

EXPERIMENTAL

A concentrated solution of Schuchardt's stannic chloride was prepared in water, in presence of dilute hydrochloric acid, and hydrated stannic oxide was precipitated by the addition of Merck's ammonia solution. The precipitate was washed in a Buchner's funnel, with water, till free from ammonia. The precipitate could not be washed free from traces of chloride ions, as on continued washing stannic oxide began to pass out as a colloid. The precipitate was then transferred to a Jena bottle and the total volume raised to about a litre. The suspension was then made homogeneous by vigorous shaking. 10 c.c. of the suspension was evaporated on a water bath, and finally heated on a blast lamp and weighed as stannic oxide. The amount of chloride in the suspension was also estimated volumetrically.

Concentration of stannic oxide in the suspension = 33.52 g. per litre
= 0.2225 gram atoms of tin per litre.

Amount of chloride in the suspension = 0.00149 gram ions of
chloride per litre.

To 2 c.c. of the homogeneous suspension were added different volumes of M/100 sodium hydroxide or sulphuric acid solution, measured from a microburette, to the total volumes raised 5 c.c. and 5 c.c. or M/100 potassium ferrocyanide solution were added. The mixtures were shaken thoroughly and kept overnight. They were then filtered and washed till the filtrates were free from ferrocyanide. The precipitates on the filter paper were moistened with 5 c.c. of a dilute ferric chloride solution, and the colours of the precipitates were noted, when the ferric chloride solution had passed out of the filter. In the tables below, the observations are recorded.

TABLE I

Final concentration of the acid or the alkali in the mixture	...	Colour of the precipitate
$2.5 \times 10^{-4} \text{M NaOH}$...	Colourless
2.0 do.	...	"
1.5 do.	...	"
1.0 do.	...	"
0.5 do.	...	Light blue
Neutral	...	Blue
$0.5 \times 10^{-4} \text{M H}_2\text{SO}_4$...	"
1.0 do.	...	"
1.5 do.	...	"
2.0 do.	...	"
2.5 do.	...	"

The same experiment was repeated with silver nitrate solution of M/10 strength as an adsorbate. The precipitates after washing were tested with potassium chromate solution.

TABLE II

Final concentration of the acid or the alkali in the mixture	...	Colour of the precipitate
$2.5 \times 10^{-4} \text{M NaOH}$...	Deep red
2.0 do.	...	"
1.5 do.	...	"

Final concentration of the acid or the alkali in the mixture		Colour of the precipitate
$1.0 \times 10^{-4} \text{M NaOH}$...	Light red
0.5 do.	...	"
Neutral	...	"
$0.5 \times 10^{-4} \text{M H}_2\text{SO}_4$...	"
1.0 do.	...	"
1.5 do.	...	"
2.0 do.	...	"
2.5 do.	...	"

It was already observed that the quantity of the acid or the alkali introduced in the systems were unable to bring about any dissolution of the stannic oxide, which could be detected in the filtrate by hydrogen sulphide. It might however be argued, that a small quantity of silver hydroxide precipitates in alkaline medium, which combines with stannic oxide to form silver stannate. Hence the adsorption of acid and basic dyes by the precipitate were also noted. The dyes used were respectively 0.1 per cent solutions of orange II and Methylene blue. To the precipitates, suspended in media of different hydrogen ion concentrations, were added 2 c.c. of the dye solutions, total volume kept 10 c.c., and the precipitates filtered the next day. The washing was done till the filtrates were free from the dyes, and the colour of the precipitates examined. The observations are recorded in tables III and IV.

TABLE III

Adsorption of Orange II.

Final concentration of the acid or the alkali in the mixture		Colour of the precipitate
$2.5 \times 10^{-4} \text{M NaOH}$...	Colourless
2.0 do.	...	"
1.5 do.	...	"
1.0 do.	...	"
0.5 do.	...	"
Neutral	...	Slightly orange
		"

Final concentration of the acid or the alkali in the mixture		Colour of the precipitate
$0.5 \times 10^{-4} \text{M H}_2\text{SO}_4$...	Slightly orange
1.0 do.	...	"
1.5 do.	...	"
2.0 do.	...	"
2.5 do.	...	"

TABLE IV

Adsorption of Methylene blue.

Final concentration of the acid or the alkali in the mixture		Colour of the precipitate
$2.5 \times 10^{-4} \text{M NaOH}$...	Blue
2.0 do.	...	"
1.5 do.	...	Light blue
1.0 do.	...	Colourless
0.5 do.	...	"
Neutral	...	"
$0.5 \times 10^{-4} \text{M H}_2\text{SO}_4$...	"
1.0 do.	...	"
1.5 do.	...	"
2.0 do.	...	"
2.5 do.	...	"

The observations, recorded in tables I to IV, show that the adsorption of basic groups are pronounced when the concentration of alkali is higher than $1 \times 10^{-4} \text{M}$ and the acid groups are adsorbed preferentially when the alkali concentration is lower than this value or when the solution is acidic. Thus this value represents the isoelectric point of the hydrated stannic oxide studied in this paper.

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STUDIES IN ADSORPTION INDICATORS : PART II


Dyes derived from Cinchomeronic acid and Quinolinic acid as adsorption indicators in argentometric titrations

BY R. C. MEHROTRA


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Following the discovery of Fajans¹, a good amount of work has been done with phthaleins, sulphonphthaleins and a few other dyes as adsorption indicators : the most studied dye in the field has been fluorescein or resorcinol-phthalein. This communication describes the use of corresponding dyes from quinolinic and cinchomeronic acids and during the course of this work, a number of observations, which are of importance, both theoretical and practical, have been made.

Preparation of the indicator dyes: Quinolinic acid,  was

prepared by the method of Ghosh² and the pure product was condensed with resorcinol. The dye had the melting point 266-267° C.

Cinchomeronic acid,  was condensed with resorcinol

and the pure dye was prepared by the method of Tewari³. The resorcinol cinchomeronein so prepared had the melting point 200°C.

Indicator solution: 0.2 gram of each dye was dissolved in 100 c.c. of 80% alcohol, and this solution was used throughout the course of this investigation.

Titration of chloride against silver ions: When the solutions have a concentration of about 0.1N, coagulation occurs just at the end point in the quinolein and just before the end point in the case of cinchomeronein. The end point (light pink→deep pink) is quite sharp in both the cases. Two drops of the indicator are sufficient for every 20 c. c. of

the titration mixture. When the solutions have a concentration below 0.02N, the end point is not so very sharp.

An observation of both practical as well as theoretical importance is that both these dyes (particularly quinolein) can be used in the above titration in presence of acid as well as alkali. No indicator for chloride ions has been mentioned in the literature so far which can be used in presence of ammonia (the concentration of ammonia being as high as 0.02 to 0.03 N in the titration mixtures studied). The presence of ammonium salts did not mask the end point. End points in presence of about 0.1N acetic acid or nitric acid are not so very sharp, but with a little experience, titration may be carried out within a reasonable accuracy (0.5%). The end points in presence of ammonia are particularly sharp. Thus the indicator can be used for a very wide range of hydrogen ion concentration, *i. e.*, when pH of the solution ranges from about 2 to 12.

These observations cannot be explained fully by the views of Fajans (*loc. cit.*) and of Kolthoff⁴ regarding the mechanism of the colour change occurring in these indicators. In their paper on dichlorofluorescein, Kolthoff and co-workers⁵ found that their indicator (dichlorofluorescein) could be applied in acidic solutions, whereas fluorescein could not be used; and they explained this difference by stating that the dichlorofluorescein itself has a stronger acid character than fluorescein and that its greater acidic nature allows it to give the end point in acid solutions, whereas the weakly acid fluorescein fails. The present indicators may be clearly expected to be much less acidic, having in their structure the basic pyridine nucleus in place of the benzene nucleus; but they give the end point, whereas the fluorescein fails to give any colour change in the acidic media. This observation is not in accord with the explanation offered by Kolthoff for the applicability of his indicator in acidic solutions. In a subsequent paper, I shall discuss this matter further.

The applicability of the present indicators in ammonical solutions does not appear to be in accord with the Fajans' theory of secondary adsorption of dye anions on the positively charged surface of the precipitate. After the end point of the titration had been reached, the supernatant liquid was decanted off and a few drops of ammonia (about 2 N) were added on to the washed pink precipitate. If the dye anions were

in a state of secondary adsorption, then the ammonia should have had a tendency to remove both the adsorbed silver and the fluoresceinate ions from the surface readily and the colour of the precipitate should have disappeared. On the other hand, the colour was intensified, particularly, in the case of the quinolein and though the particles went on diminishing in size, but the colour on the particles remained.

Moreover, the applicability of the indicators in ammoniacal solutions has a great technical importance. In mints etc., where the determination of silver has to be done as a routine process, the preparation of neutral solutions is very tedious. With these indicators, the titration can be easily carried out by taking acidic solutions and making them ammoniacal by the addition of excess ammonia and then titrating.

Titration of sulphocyanide against silver ions: In concentrated solutions (about 0.1 N), coagulation begins with the first drop of silver nitrate and the coagulated particles assume a slight pinkish colour; but at the end point, there is a sharp colour change, (light pink \rightarrow deep pink), on the coagulated precipitate. The end point is not masked by the addition of ammonia and titrations can be carried out with a little care in ammoniacal and acidic solutions. The titrations are completely reversible and suitable upto 0.01 N dilutions.

Titration of bromide against silver ions: The indicators are quite suitable for dilutions upto 0.01 N. The coagulation occurs just at the end point, and so, just at the point when the equivalent amount of silver nitrate has been added, there is the transference of yellowish pink colour from the solution to deep pink colour on the coagulated precipitate. The titration is not possible in presence of ammonia, and the pink colour on the washed precipitate of silver bromide after the end point is removed by the addition of a few drops of dilute ammonia solutions. The end points are not so sharp in presence of acids also, but the titrations can be easily carried out upto a pH = 6. Moreover, the titrations are quite reversible in dilute solutions.

Titration of iodide against silver ions: Here, again, these indicators have been found of great practical value. They can be used for iodide ions from a concentration of 0.1 N to 0.001 N. In more concentrated solutions, the coagulation occurs at the end point, so the point is indi-

cated by the transference of pink yellow colour in the liquid phase to the deep pink colour on the precipitate. In dilute solutions, however, no coagulation of the precipitate occurs and so the end point is indicated by the whole of the liquid phase changing colour from pinkish yellow to deep pink. The end point is very sharp upto dilutions of 0.001 N. In dilute solutions, the titrations are completely reversible, *i. e.*, if a little excess of silver nitrate solution be added, a known volume of the iodide solution may be again added on to the same titration mixture, and as soon as iodide ions are in excess, the liquid phase again becomes yellow; and so the titration can now be completed with silver ions.

Volume and conc. of halide solutions	Drops of indicator	Volume and conc. of AgNO_3 solutions	Transition of colour	Remarks
10 c.c. of N/10 KCl	2	9.96 to 9.98 c.c. of N/10 AgNO_3	Light Pink → Deep Pink	In the case of cinchomeronein, the colour change occurs on the coagulated precipitate. In the case of quinolein, colour change occurs from liquid to solid phase. The end point is very sharp in both the cases.
10 c.c. of N/10 KCl + 4 c.c. of 0.2 N Ammonia	2	9.98 to 10.01 c.c. of N/10 AgNO_3	Pink Soln. → Deep Pink ppt.	Coagulation occurs just at the end point which is quite sharp.
10 c.c. of N/10 KCl + 2 c.c. N HAc or HNO_3	2	10 to 10.04 c.c. of N/10 AgNO_3	Colourless soln. → light pink ppt.	The end points are not so sharp.
10 c.c. of N/10 KCNS	2	10 to 10.02 c.c. of N/10 AgNO_3	Light Pink ppt. → Deep Pink ppt.	Coagulation begins with the first drop of silver nitrate but there is a sharp end point.
10 c.c. of N/10 KCNS + 1 c.c. of 0.2 N Ammonia	1	10 to 10.07 c.c. of M/10 AgNO_3	Light Pink solns. → Pink ppt.	Colour change is not so sharp.
10 c.c. of N/10 KCNS + 1 c.c. of NHAc	3	10 to 10.05 c.c. of N/10 AgNO_3	Colourless solution → Pink ppt.	Colour change is not so very sharp.

Volume and conc. of halide solutions	Drops of indicator	Volume and conc. of AgNO_3 solution	Transition of Colour	Remarks
10 c.c. of N/100 KBr	1	10 to 10.04 c.c. of N/100 AgNO_3	Pinkish yellow soln. \rightarrow Pink ppt.	Colour change is very sharp at the end point.
10 c.c. of N/10 KI	2	10 to 10.02 c.c. of N/10 AgNO_3	Yellow ppt. \rightarrow Pink ppt.	Very sharp end point.
10 c.c. of N/1000 KI	1	10 to 10.04 c.c. of N/1000 AgNO_3	Yellow ppt. \rightarrow Pink soln.	Colour change in the liquid phase is very sharp. The titration is completely reversible.

Further work with the indicators is in progress.

I wish to thank Dr. J. D. Tewari, D. Sc., for the preparation of dyes and Prof. N. R. Dhar for his interest throughout this work.

SUMMARY

1. The dyes resorcinol-quinolein and cinchomeronein have been found to be very suitable indicators for argentometric titrations.
2. Their great usefulness lies in their ability to indicate the end point in titrations of chloride ions against silver ions in both acidic as well as ammoniacal media.
3. The possibility of titrations in presence of ammonia will make the process much less tedious in technical determinations of silver.
4. The applicability of these indicators in acidic and ammoniacal solutions cannot fully be explained by the present views about mechanism of the colour change of the adsorption indicators.
5. In the case of iodide ions, the titrations are possible upto a dilution of 0.001 N solutions.

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INVESTIGATION OF THE KINETICS OF REDUCTION BETWEEN RESORCIN AND SILVER TARTRATE IN THE LIGHT OF CATALYTIC ACTIVITY OF COLLOIDAL SILVER

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The importance of colloidal silver in the reduction of silver salts has been emphasized by several workers (1, 2, 3, 4, 5, 6, 7). In this paper the kinetics of reduction of silver tartrate has been described which serves to illustrate the mechanism of the reaction between resorcin and silver tartrate.

EXPERIMENTAL

A precipitate of silver tartrate is prepared by adding a solution of sodium tartrate to a solution of silver nitrate. This is washed several times with water to free it from adsorbed ions. It is then dissolved in water. The strength of this solution is determined by titrating against a standard potassium chloride solution using potassium chromate as an indicator.

A known volume of this solution is taken in a dark reaction bottle which is kept in a bath maintained at a constant temperature. The reaction is started by adding a known volume of resorcin solution to the solution of silver tartrate. Previous to addition of resorcin, known volumes of distilled water, starch solution and sodium acetate are added in such a way that the total volume is always 100 c. c.

Now at definite intervals of time 10 c. c. of the reaction mixture are taken and added to 5 c. c. of M/25 potassium chloride solution. To this, a few crystals of potassium nitrate are added to precipitate the colloidal silver formed during the reaction. From the filtrate 5 c. c. are taken and titrated against standard solution of silver nitrate, using potassium chromate as an indicator. The infinity reading is found out by calculation where the reaction is very slow, and by direct observation where it is fast.

Total Order and Temperature Coefficient.—The concentration of resorcin is kept several times greater than that of silver tartrate. At first the value of the unimolecular velocity constant is determined at a particular

concentration of resorcin and then at half this concentration. The concentration of silver tartrate is identical in both the cases. It will be seen that the value of velocity constant goes on decreasing. This decrease is due to a gradual precipitation of colloidal silver which acts as a catalyser and also to a decrease in the pH of the reaction mixture.

TABLE I

Temperature 50°C		
	Silver tartrate (N/82.5)	50 c.c.
	Resorcin (16%)	20 c.c.
	Water	30 c.c.
		100 c.c.
Time in minutes	Vol. of Silver nitrate (N/24.75) used	K_1 unimolecular
0	1.20 c.c.	...
5	1.23 c.c.	0.013800
10	1.25 c.c.	0.011653
20	1.27 c.c.	0.008441
40	1.29 c.c.	0.005571
100	1.35 c.c.	0.004050
200	1.39 c.c.	0.002739
400	1.44 c.c.	0.001903
Infinity	1.65 c.c.	...

TABLE II

Temperature 50°C		
	Resorcin (8%)	20 c.c.
	Silver tartrate (N/91)	50 c.c.
	Water	30 c.c.
Time in minutes	Volume of N/24.75 silver nitrate used	K_2 unimolecular
0	1.24 c.c.	...
10	1.26 c.c.	0.004991
20	1.28 c.c.	0.005679
40	1.31 c.c.	0.006574
100	1.37 c.c.	0.003708
200	1.40 c.c.	0.002470
300	1.43 c.c.	0.002073
500	1.47 c.c.	0.000844
Infinity	1.65 c.c.	...

In table II, we observe a slight induction period which suggests silver catalysis. After reaching a maximum, the velocity constant again begins to decrease. This decrease is to be ascribed to a gradual precipitation of colloidal silver and also to some extent to an increase in the acidity of the reaction mixture.

TABLE III

Temperature 40°C

	Silver tartrate (N/90)	50 c.c.
	Resorcin (8%)	20 c.c.
	Water	30 c.c.
Time in minutes	Volume of N/24.45 silver nitrate used	K ₃ unimolecular
0	1.25 c.c.	...
10	1.25 c.c.	0.000000
22	1.27 c.c.	0.0027605
40	1.29 c.c.	0.002732
100	1.32 c.c.	0.002035
200	1.34 c.c.	0.001311
Infinity	1.63 c.c.	...

Table III shows a marked induction period. This suggests the auto-catalytic nature of the reaction. It further shows that the reaction is unimolecular with respect to silver salt.

Calculation of the Order and Temperature Coefficient.—The velocity of the reaction in the first table is given by :

$$\left(\frac{dx}{dt}\right)_1 = K \times C_R^{n_1} \times C_{Ag}^{n_2} = K_1 C_{Ag}^{n_2}$$

where

 C_R = concentration of resorcin

 C_{Ag} = concentration of silver salt

and n_1 and n_2 denote molecularity with respect to resorcin and silver

Similarly in table II :

$$\left(\frac{dx}{dt}\right)_2 = K \left(\frac{C_R}{2}\right)^{n_1} \times C_{Ag}^{n_2} = K_2 C_{Ag}^{n_2}$$

Now,

$$K_1 = K C_R^{n_1}$$

and

$$K_2 = K \left(\frac{C_R}{2}\right)^{n_1}$$

where K is the true velocity constant of the reaction.

$$\text{Now } \frac{K_1}{K_2} = \frac{2^{n_1} C_R^{n_1}}{C_R^{n_1}} = 2^{n_1}$$

from which n_1 can be calculated. In the present case it works out to be 1.06.

$$\therefore \text{Total order} = 1.06 + 1 = 2.$$

In all calculations, the highest values of the velocity constants have been used.

Temperature Coefficient. Comparing the highest values of the velocity constants in tables II and III, we find that the temperature coefficient of the reaction for 10 degrees is 2.5 approximately.

Effect of adding colloidal silver. Uptil now the evidence in favour of the catalytic activity of silver has been indirect. Table IV and V show that by directly adding colloidal silver, the values of the velocity constants increase to a great extent. Starch is added to stabilise colloidal silver. In itself starch does not affect the velocity constant.

The silver sol, used in these experiments, was prepared by passing a current of hydrogen into a saturated solution of silver citrate containing some silver citrate in suspension also. The reaction was carried out at about 80°C till no silver ions were found in the solution. This was tested by precipitating the colloidal silver with KNO_3 and testing the supernatant liquid for silver ion. The solution, thus prepared, contained 0.5 gms. of silver per litre. The electrical conductivity of the solution was of the order of 10^{-5} mhos. The only possible impurity is citric acid which has no reducing action on silver ion. Further, it was noted that the silver sol by itself shows no reduction action on silver tartrate.

TABLE IV

Temperature 50°C

Silver tartrate (N/83.0)	50 c.c.
Resorcin (16%)	20 c.c.
Colloidal silver	27 c.c.
Starch (1%)	3 c.c.

Time in minutes	Volume of N/24.75 silver nitrate used	Velocity constant
0	1.12 c.c.	...
5	1.20 c.c.	0.032706
10	1.23 c.c.	0.023253
20	1.27 c.c.	0.011078
40	1.31 c.c.	0.011071
100	1.37 c.c.	0.006373
200	1.40 c.c.	0.003753
400	1.45 c.c.	0.002433
Infinity	1.65 c.c.	...

TABLE V

Temperature 50°C

	Silver tartrate (N/87)	50 c.c.
	Colloidal silver	27 c.c.
	Starch (1%)	3 c.c.
	Resorcin (8%)	20 c.c.
Time in minutes	Volume of N/24.75 silver nitrate used	Velocity constant
0	1.14 c.c.	...
10	1.21 c.c.	0.014763
20	1.26 c.c.	0.013897
40	1.28 c.c.	0.008265
100	1.31 c.c.	0.007530
200	1.36 c.c.	0.002869
300	1.38 c.c.	0.001784
500	1.41 c.c.	0.001480
Infinity	1.65 c.c.	...

When we compare tables I and IV, and II and V, we at once perceive the effect of adding colloidal silver. The unimolecular velocity constants have increased 2 to 3 times and the induction period has completely disappeared.

Hydrogen ion concentration effect.—As the reaction progresses, the concentration of hydrogen ions goes on increasing. These act as retarding agent, and a gradual fall in the velocity constant is also due to this factor. The increase in acidity is due to the oxidation of resorcinol into some organic acid.

TABLE VI

Temperature 40°C

	Silver tartrate (N/81)	50 c.c.
	Resorcin (16%)	20 c.c.
	Sodium acetate 0.25 gm. in	30 c.c.
		of water
Time in minutes	Volume of N/14.6 silver nitrate used	Velocity constant
0	1.06 c.c.	...
3	1.08 c.c.	0.011653
5	1.09 c.c.	0.010180
10	1.15 c.c.	0.015214
20	1.18 c.c.	0.011569
40	1.23 c.c.	0.008659
100	1.35 c.c.	0.0069230
200	1.45 c.c.	0.006229
400	1.55 c.c.	...
Infinity	1.64 c.c.	...

A perusal of the above table shows that the addition of sodium acetate has increased the value of velocity constant. We expect that at 40°C and with resorcin of 16% strength, the velocity constant cannot be greater than 0.005, but here we find the highest value of the constant to be equal to 0.01569. The fact is that due to the addition of sodium acetate, the pH of the solution is raised and hence the reaction is faster.

On the other hand, we find that in spite of adding sodium acetate, (which checks the increase in acidity) the fall in velocity constant is still there. This is due to the fact, that fall in the constant is more to be ascribed to a gradual precipitation of silver rather than to an increase in hydrogen ion concentration.

If we use larger concentrations of sodium acetate, the velocity of the reaction increases and the reaction completes itself in about 100 minutes. The reaction is almost complete before the colloidal silver precipitates out. Here, therefore, we find, that the value of the velocity constant does not decrease. (See table VIII).

TABLE VII

Temperature 40°C

Concentrations are the same as in table VI, with 2 grams of sodium acetate.

Time in minutes	Velocity constant
0	..
5	0.021970
10	0.023350
20	0.025194
40	0.02348
100	0.028718
200	...

Effect of adding ammonium sulphate.—When ammonium sulphate is added to the reaction mixture, the velocity of the reaction falls down to a considerable extent. This is apparent from the following table.

TABLE VIII

Temperature 40°C

	Silver tartrate	50 c.c.
	Resorcin (16%)	20 c.c.
	Water	30 c.c.
	Ammonium sulphate	1 gm.
Time in minutes	Volume of N/24.6 Silver nitrate used	
0	1.05 c.c.	
10	1.06 c.c.	
20	1.08 c.c.	
40	1.09 c.c.	
100	1.11 c.c.	
230	1.12 c.c.	
400	1.14 c.c.	
Infinity	1.64 c.c.	

CONCLUSION AND DISCUSSION

Our experimental results conclusively prove that silver in the colloidal state exerts catalytic action. Further, this catalysis is greater, the smaller the size of the particles. This is evident from a fall in the velocity constant of the reaction.

We further suggest the following mechanism of reaction in the reduction of organic salts of silver.

At first, silver hydroxide is produced by the hydrolysis of silver salt, as the intermediate compound; and since it is most readily reducible, the reaction proceeds. Now in the presence of excess of hydrogen ions, the hydrolysis of silver salts is checked, and thus hydrogen ions act as retarding agent. This shows why the reaction proceeds much more quickly in the alkaline medium. The hydroxyl ions, on the one hand, serve to remove hydrogen ions, and on the other, produce silver hydroxide.

If we take a solution of silver tartrate and add to it a solution of sodium hydroxide, at first silver hydroxide is produced, which then gets reduced by tartrate ions. In this way, beautiful sols of silver can be produced.

If we take a solution of silver tartrate and add to it a suspension of silver hydroxide with a little of sodium acetate, the hydroxide gets reduced, and metallic silver is formed. These experiments show, that silver hydroxide is very much susceptible to reduction and is the most probable intermediate product in the reduction of silver salts.

SUMMARY

(1) The reaction between silver tartrate and resorcin is bimolecular. It is unimolecular with respect to each reactant separately.

(2) The reaction is positively catalysed by colloidal silver and negatively by hydrogen ions.

(3) The reduction of silver salt is most probably preceded by hydrolysis of the salt into silver hydroxide and the corresponding acid.

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EFFECT OF THE EXCESS OF THE PRECIPITANT ON THE NATURE OF THE PRECIPITATE OBTAINED*

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During the course of a systematic work for finding out the change involved in the transformation of blue hydrated cupric hydroxide to the black one, the effects of varying the conditions of precipitation on the nature of the precipitate obtained were studied.

An observation has been made by precipitating copper hydroxide under the following three conditions :—

1. Slight excess of copper ions.
2. Equivalent amounts of copper and hydroxyl ions.
3. Slight excess of hydroxyl ions.

The three precipitates, thus obtained, exhibit a marked variation in their physical characteristics and chemical properties. If the precipitates are allowed to stand in contact with their mother liquors for a short time, and then washed free from all electrolytes, the three precipitates will show a variation in their colour from blue, brown to deep brownish black. Also, if equal amounts of each type of precipitate are shaken with and allowed to stand for a few days in contact with the same concentration of ammonium hydroxide solution, they will exhibit a decreasing order of solubility in ammonia, *i.e.*, the copper hydroxide, obtained from a slight excess of copper ions, will show the greatest solubility and will develop the deepest blue colour with ammonia, the second one will exhibit much less solubility than the first, while the solubility, as well as the colour of the solution obtained from the third, will be slightly lesser than those of the second. This variation in the properties of the different samples of copper hydroxide, became much more marked when the precipitates are allowed to age with their mother liquors.

It may be urged that the greater solubility of the first one is due to its being present as a basic salt. H.T.S. Britton¹ has reported that

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copper is completely precipitated as a basic hydroxide even when only 1.5 equivalents of the alkali have been added per mole of the copper sulphate. In order to decide whether the above mentioned variation in the properties of hydrated copper hydroxide is merely due to the basic salt formation, a simple test was applied. The excess of copper ions added in the first case was varied, but as the results show, this variation did not produce any noticeable difference in the solubility of the obtained precipitate. Theoretically also, the small amounts of basic salt, even if present, would be converted, under the conditions, into the hydroxide by the hydroxyl ions from ammonia without affecting, to any appreciable extent, the concentration of ammonia itself.

EXPERIMENTAL

A standard semi molar solution of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and a normal solution of caustic soda were prepared and the following amounts of the two solutions were mixed :

A(1) 22.0 c.c. of copper sulphate and 20.0 c.c. of caustic soda solutions.

A(2) 21.5 c.c. of " " and 20.0 c.c. of " " "

A(3) 21.0 c.c. of " " and 20.0 c.c. of " " "

B. 20.0 c.c. of " " and 20.0 c.c. of " " "

C(1) 20.0 c.c. of " " and 21.0 c.c. of " " "

C(2) 20.0 c.c. of " " and 22.0 c.c. of " " "

Each of the above precipitates was allowed to stand for 4 to 6 hours in contact of their mother liquors. After digestion with the mother liquor, the precipitates were well washed free from all electrolytes and then, each of them was suspended in 200 c.c. of distilled water. Each suspension was well stirred and 50 c.c. of the suspension was taken and added to each of three 100 c.c. flasks containing different volumes of 2.0N NH_4OH , that on the volume in each flask being made upto 100 c.c., the concentrations of ammonium hydroxide was respectively 1.0 N, 0.5 N, and 0.4 N. These suspensions were allowed to stand for about 48 hours and were then analysed. The suspensions from A were much more blue than those from B ; while those from C were slightly lesser blue in shade than those from B. The clear ammoniacal solution, 10.0 c.c. in each case, was pipetted off, neutralised with a slight excess of acetic acid and excess of potassium

iodide added. The iodine liberated was titrated against standard thiosulphate solution. The following results were obtained :—

Sample	1.0NH ₄ OH	0.5NH ₄ OH	0.4NH ₄ OH
Sample A(1)	18.7 c.c. of M/100 thiosulphate	18.1 c.c. of M/200 thiosulphate	22.5 c.c. of M/400 thiosulphate
Sample A(2)	18.8 c.c. ,,	17.8 c.c. ,,	22.3 c.c. ,,
Sample A(3)	18.6 c.c. ,,	17.9 c.c. ,,	22.6 c.c. ,,
Sample B	17.7 c.c. ,,	14.9 c.c. ,,	15.8 c.c. ,,
Sample C(1)	16.6 c.c. ,,	13.4 c.c. ,,	12.8 c.c. ,,
Sample C(2)	16.7 c.c. ,,	13.2 c.c. ,,	12.9 c.c. ,,

The above table shows that the three types of hydroxides show different solubilities in ammonium hydroxide solutions. As is evident from the above data, the difference is much more marked in the dilute solutions of ammonia and tends to become much less as the concentration of the ammonia solution is increased. We are of the opinion that this difference in behaviour of differently precipitated cupric hydroxide is due to the difference in the sign and magnitude of the charge on the particles due to preferential adsorption of the ions of the mother liquor during the process of the digestion of the precipitate. This difference in the electrical charge on the particles of the precipitates exhibits itself by the decreasing peptisability of the particles by dilute ammonia solutions. The existence of colloidal matter in the solutions of cuprammines has, from time to time, been demonstrated by several workers². Sen and Dhar³ have shown on the basis of cataphoretic and electrical conductivity experiments, that the blue solutions of copper hydroxide in ammonia contain a fair amount of the substance in colloidal conditions. With increasing concentrations of ammonia, the effect of this intermediate colloidal state of the hydroxide, peptised by ammonia, diminishes and the true molecular complex formation is much more pronounced and hence, the difference in the solubilities of the different samples is much less marked in concentrated ammonia solutions.

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